AMBIENT GROUNDWATER QUALITY OF THE DOUGLAS BASIN:

A 1995-96 BASELINE STUDY

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1. ABSTRACT

The Groundwater Monitoring Unit of the Arizona Department of Environmental Quality (ADEQ) completed a baseline groundwater quality study of the Douglas Groundwater Basin (DGB) in 1995-96. A total of 51 groundwater samples were collected for the study, whose design included 29 grid-based, stratified random samples and 21 targeted samples. All groundwater samples were analyzed for Safe Drinking Water (SDW) inorganics, 12 samples were analyzed for SDW Volatile Organic Compounds (VOCs), 7 samples were analyzed for Groundwater Protection List (GWPL) pesticides, and 6 samples were analyzed for radionuclides. Laboratory results revealed no detections of any GWPL pesticides while the only SDW VOC detected was chloroform in 1 sample. Radionuclide samples did not exceed Primary Maximum Contaminant Levels (MCLs) for any parameter. With inorganic parameters, levels of arsenic, beryllium, and nitrate each exceeded their respective health-based Primary MCLs in 1 sample apiece. Aesthetics-based Secondary MCLs were exceeded in 16 samples: 8 times by fluoride and total dissolved solids (TDS), twice by pH and sulfate, and once by chloride, iron, and manganese. These results suggest that regional groundwater quality conditions generally support drinking water uses, but because of aesthetic factors, some residents may prefer to use treated water for domestic purposes.

Piper trilinear diagrams reveal that of the 2 major aquifers in the DGB, bedrock aquifer samples tend to exhibit a calcium-bicarbonate chemistry; alluvial aquifer samples also typically exhibit a calcium-bicarbonate chemistry though sodium-bicarbonate, sodium-sulfate, and calcium-sulfate varieties are also present in this aquifer. Statistical analyses found that many significant differences exist in inorganic groundwater quality parameter levels between aquifers while fewer differences existed between groundwater management areas, and between various divisions (East-West, North-South) of the DGB. A strong positive correlation existed between the levels of most major ions and nitrate; in contrast, fluoride and pH tend to be negatively correlated with other groundwater quality parameters while trace elements have few significant correlations. Many parameter levels also significantly increased or decreased with increasing groundwater depth below land surface in the DGB.

Comparing parameter levels from targeted samples with 95% confidence intervals established for the DGB indicated several potential impacts. Nitrate appears to be elevated in the Elfrida area perhaps from agricultural practices and/or septic systems. Near the City of Douglas, high sodium and pH levels in combination with low calcium and magnesium levels appear to indicate groundwater is being subjected to natural softening by cation exchange. Elevated sulfate levels in the Mule Gulch area might be the result of mine tailings in the area. Finally, a geothermal anomaly appears to exist east of the Bisbee-Douglas Airport resulting in TDS levels reaching 14,000 mg/l and elevated levels of temperature, arsenic, and other parameters.

A time-trend analysis was conducted using groundwater quality data collected by ADWR from 7 wells in 1987. The results indicated while many of the 12 parameters appeared to have higher levels in 1995-96 than 1987, only nitrate and potassium were significantly higher.

2. OBJECTIVES

The Groundwater Monitoring Unit (GMU) of the Arizona Department of Environmental Quality (ADEQ) conducted an extensive regional groundwater quality study of the Douglas Groundwater Basin (DGB) in 1995-96. The impetus for this groundwater study was threefold:

- An ADEQ report (Hood, 1991) which, in evaluating the need for ambient monitoring in each of the 50 designated groundwater basins in Arizona, ranked the DGB as the 8th highest basin priority for the collection of groundwater quality data;

- Because of recent population growth and the associated increase in well drilling, an opportunity to collect groundwater samples from portions of the basin that could not be sampled by previous studies; and

- Support the data collection and hydrologic analysis requirements of the ADEQ Watershed Program for the Upper San Pedro Watershed.

This groundwater study had five objectives:

- To obtain baseline data throughout the DGB on the occurrence, concentrations, and ranges of a wide array of groundwater quality parameters including the identification and delineation of any areas with elevated groundwater quality parameter levels.

- With the sampling sites determined through means of stratified random selection, to examine particular geographic areas and aquifers within the DGB for statistically significant groundwater quality differences.

- Using the sampling sites determined through means of stratified random selection, examine relationships with groundwater quality parameter levels and indices such as groundwater depth and other groundwater quality parameter levels.

- Using groundwater quality data collected during previous studies by other government agencies, resample some of the same wells in order to examine temporal groundwater quality trends in the DGB.

- To establish a statistically designed ambient groundwater quality index well monitoring network for the DGB.

Meeting these objectives in a reproducible, scientific study that utilizes statistical analysis to make broad statements concerning groundwater quality will provide many benefits.

- Residents in the DGB utilizing water supplied by a public water system for domestic purposes have the assurance that this resource is tested regularly and meets water quality standards set by the Safe Drinking Water (SDW) Act. However, many rural residents are served by private wells whose water is seldom tested for a wide variety of possible pollutants. While Arizona statutes require well drilling contractors to disinfect new wells which are used for human consumption for potential bacteria contamination, many wells are not further tested for other types of groundwater quality problems. Thus, contamination affecting groundwater pumped from private wells may go undetected for years and have adverse health effects on users of this resource. While collecting and analyzing groundwater samples from all these private wells would be prohibitively expensive, a statistically-based ambient groundwater study to estimate groundwater quality conditions on a regional scale and identify possible associations with landscape attributes to help explain impaired groundwater conditions offers an affordable alternative.

- Determining whether groundwater in the DGB is currently suitable for domestic and municipal uses.

- Provides a scientific basis for distinguishing pollution impacts to aquifers.

- Assessing the effectiveness of groundwater protection efforts such as industry Best Management Practices (BMPs) by tracking groundwater quality changes.

- Be a useful tool with which to guide DGB planning and new public water supply well locations and determine wellhead protection areas.

- Provide reliable and consistent information on the status and trends in the quality of the groundwater resources of the DGB.

10. CONCLUSION

This 1995-96 ADEQ regional study to assess the groundwater quality of the DGB had 6 major objectives:

- Obtain baseline data throughout the basin on the occurrence, concentrations, and ranges of a wide array of groundwater quality parameters;

- Characterize groundwater quality differences between various spatial areas;

- Examine relationships with groundwater quality parameter levels and indices such as groundwater depth and other groundwater quality parameter levels;

- Assess the impact on groundwater quality from potential contaminant sources related to specific land uses and/or management practices;

- Conduct a groundwater quality time-trend analysis using results from previous studies for baseline data; and

- Establish an ambient monitoring index well network for long-term examination of temporal groundwater quality trends.

The results of the study indicated the following key findings for each objective:

Obtain baseline data throughout the basin on the occurrence, concentrations, and ranges of a wide array of groundwater quality parameters

Overall, the groundwater quality of the DGB is generally acceptable for drinking and other domestic uses based on the results of this study. Some residents may prefer to use treated or filtered water because of poor aesthetic characteristics such as taste, smell, and/or color of the groundwater occasionally encountered in the DGB. This conclusion is based on the following findings:

- Only 3 of the 51 groundwater samples collected for the DGB study had exceedences of health-based, inorganic Primary MCLs (**Figure 7**). These 3 exceedences were for As, Be, and NO_3-N (**Figure 8**, **9**, and **10**), with each exceeding its respective Primary MCL in 1 sample. The DGB groundwater samples were tested for 13 inorganic parameters having Primary MCLs, though Sb results were considered invalid due to groundwater filter contamination problems.

- Sixteen of the 51 DGB groundwater samples had exceedences of aesthetics-based, inorganic Secondary MCLs (**Figure 7**). This indicates that approximately one-third of the groundwater samples collected for this study had aesthetic problems with indices such as taste, odor, and/or color. The groundwater samples were tested for 10 inorganic parameters having Secondary MCLs and the following exceedences occurred: Cl - 1, F - 8, Fe - 1, Mn - 1, pH-field - 2, pH-lab - 2, SO_4 - 2, and TDS - 8 (**Figure 9**, **11, 12**, and and **13**).

- Results from the 29 randomly sampled wells were used to created 95% Confidence Intervals ($CI_{0.95}$) for most inorganic parameters (**Table 13**).

- There were no detections of any pesticides in the 7 samples tested for GWPL analysis (see **Appendix H**). The GWPL consists of the 152 pesticides used in Arizona that are considered most likely to leach to the groundwater through normal agricultural use (see **Appendix J**). The 7 groundwater samples tested for pesticides were collected in areas of agricultural activity within the DGB.

- Of the 12 SDW VOC samples collected within the DGB, only chloroform was detected in a single sample at the MRL (**Appendix G**). The sample having this VOC detection was collected at a turbine well; therefore, the detection may have been the result of lubricants that are normally added to the well pump. The SDW VOC list is comprised of 58 VOCs that are considered the most likely potential threats to public drinking supplies (**Appendix I**). The limited sampling conducted for VOCs in the DGB was focused in likely areas of contamination such as landfills and industrial areas.

- Of the 6 groundwater quality samples collected for radionuclide analysis, none exceeded SDW Primary MCLs for Gross α, Gross ß, and Combined Radium-226+Radium-228 (see **Appendix F**). The radionuclide samples were collected in areas thought to contain elevated levels of these constituents.

Characterize groundwater quality differences between various spatial areas

Groundwater quality differences between various physical and cultural areas in the DGB were examined using 4 spatial comparisons: aquifer (alluvial - bedrock), Irrigation Non-Expansion Area (INA) Boundary (inside - outside), valley (east - west), and basin (north - south). Although significant groundwater quality parameter level differences were found with all the spatial comparisons, aquifer differences were by far the most numerous with bedrock parameter levels generally significantly greater than alluvial parameter levels. INA differences followed a similar pattern as the aquifers, while there were few valley and basin differences. Depth to groundwater bls is significantly greater in the both the alluvial aquifer and inside the INA than the bedrock aquifer and outside the INA; there are no significant differences between valley- sides and/or basin portions. These conclusions are based on the following findings:

- Significant groundwater quality parameter level differences were most numerous in comparisons between aquifers in the DGB. Generally, parameter levels were higher in the bedrock aquifer than the alluvial aquifer. Parameters such as Ca, HCO_3, hardness, Mg, SO_4, total alkalinity, and turbidity were significantly higher in the bedrock than the alluvial aquifer. In contrast, pH-field, pH-lab, and temperature-field were significantly higher in the alluvial aquifer than the bedrock aquifer (**Table 2**). Piper trilinear diagrams illustrate the different groundwater quality chemistry of the two aquifers. Bedrock groundwater samples tend to exhibit a Ca-HCO_3 chemistry while alluvial groundwater samples tend to be of either Na-HCO_3 or Ca-HCO_3 chemistries (**Figure 6**).

- Spatial patterns of groundwater quality parameter levels between INA boundaries were similar to those found with aquifers, as both the aquifer and INA demarcation lines divide the DGB into similar areas. Parameters such as Ca and turbidity were significantly higher outside the INA than inside the INA. In contrast, F, pH-field, pH-lab, and temperature-field were significantly higher inside the INA than outside the INA (**Table 3**). Groundwater samples collected outside the INA tend to exhibit a Ca-HCO_3 chemistry while groundwater samples collected inside the INA tend to be of either Na-HCO_3 or Ca-HCO_3 chemistries (**Figure 6**).

- Only 2 significant groundwater quality parameter level differences were found when using the Whitewater Draw to divide the DGB into East and West valleys; Ca was significantly higher in the West valley, pH-field was significantly higher in the East valley (**Table 4**). No water chemistry differences between valleys were apparent in plotting these groundwater samples onto Piper trilinear diagrams (**Figure 6**).

- Only 3 significant groundwater quality parameter level differences were found when dividing the DGB into North and South basins, somewhat arbitarily, at the 22 South Township line. Levels of F were significantly higher in the northern part of the DGB, while Ba and HCO_3 were significantly higher in the southern part of the DGB (**Table 5**). No water chemistry differences between basins were apparent in plotting these groundwater samples onto Piper trilinear diagrams (**Figure 6**).

- Differences in depth to groundwater bls were examined using the 4 DGB spatial comparisons previously discussed. The alluvial aquifer and the area inside the INA had significantly greater depths to groundwater bls than the bedrock aquifer and areas outside the INA, respectively (**Table 12**). There were no significant differences between valley-sides (east - west), and basin portions (north - south).

Examine relationships with groundwater quality parameter levels and indices such as groundwater depth and other groundwater quality parameter levels

The levels of some groundwater quality parameters in the DGB, especially major ions and NO_3-N, are positively correlated with one another. An exception to this trend is F and pH-field whose levels are often negatively correlated with other parameter levels. Most trace elements have few, if any, correlations with other groundwater quality parameters. Levels of many groundwater quality parameters tended to either significantly decrease or increase with increasing groundwater depth below land surface (bls) in the DGB. These conclusions are based on the following findings:

- The levels of many of the 21 groundwater quality parameter levels (56 of 210 parameter pairings) in the DGB are significantly positively correlated, especially major ions and NO_3-N. In other words, as the levels of one parameter rise, the levels of other parameters also tend to rise. There were fewer significant negative correlations (10 of 210 parameter pairings), most involving F and pH-field, in which parameter levels tended to decrease as other groundwater quality parameter levels tended to increase. Trace elements had far fewer significantly-correlated relationships with other parameters than did major ions (**Table 6**).

- In the alluvial aquifer, the levels of many of the 21 groundwater quality parameter levels (50 of 210 parameter pairings) are significantly positively correlated, especially major ions and NO_3-N. There were fewer significant negative correlations (6 of 210 parameter pairings), most involving pH-field, temperature-field, and F (**Table 7**). In the bedrock aquifer, some of the 21 groundwater quality parameter levels (33 of 210 parameter pairings) are significantly positively correlated, especially major ions and NO_3-N. There was only 1 significant negative correlation (NO_3-N - turbidity) among the parameter pairings. The only trace element with a significant correlation was Zn-K (**Table 8**).

- Ten of the 21 groundwater quality parameters examined had levels that significantly decreased or increased with increasing groundwater depth bls in the DGB. The parameters that decreased with groundwater depth bls include Ca, EC-field, hardness, SO_4, and turbidity while parameters increasing with groundwater depth bls include B, pH-field, pH-lab, K, and temperature-field (see **Table 9**). All these parameter level - groundwater depth relationships were most adequately described by a biphasic model except for Ca and temperature-field which were linear relationships.

- When analyzed by aquifer, few groundwater quality parameters examined had levels that significantly decreased or increased with increasing groundwater depth bls in the DGB. In the alluvial aquifer, turbidity decreased with groundwater depth bls while temperature-field increased with groundwater depth bls (see **Table 10**). Both of these parameter level - groundwater depth relationships were most adequately described by a biphasic model and were similar to relationships found with the overall DGB results.

- In the bedrock aquifer, the parameter that significantly decreased with groundwater depth bls was TKN while the parameters that significantly increased with groundwater depth bls were temperature-field and turbidity (see **Table 11**). While the temperature-field relationship is the same as found in both the alluvial aquifer and overall DGB results, the turbidity results are opposite what were found in both the alluvial aquifer and overall DGB results. A linear model most adequately described temperature-field and turbidity parameter level - groundwater depth relationships while TKN was described best by the biphasic model.

Assess the impact on groundwater quality from potential contaminant sources related to specific land uses and/or management practices:

Within the DGB, 6 areas were selected for additional targeted sampling to determine potential impacts from specific land uses. These areas included the Town of Elfrida, City of Douglas, Mule Gulch, Town of McNeal, Bisbee-Douglas International Airport, and northern Sulphur Springs Valley. Results from targeted samples were compared with $CI_{0.95}$ determined from stratified random sampling in the DGB. Targeted sample parameter level exceedences of the $CI_{0.95}$ were viewed as potentially being impacted. All studied areas showed potential impacts except with the intensively irrigated farmland of the northern Sulphur Springs Valley. These conclusions are based on the following findings:

- To examine for impacts from a nearby landfill, irrigated agriculture, and septic systems, 9 targeted groundwater samples were collected in the Elfrida area. As NO_3-N and pH-field were the only parameters typically exceeding the $CI_{0.95}$, there appeared to be no groundwater quality impacts from the landfill (**Table 14**). However, the NO_3-N levels in the Elfrida area indicate that septic systems and/or agricultural practices may have impacted groundwater quality in the area (**Figure 16**).

- To examine for impacts from the slag heap formed by the former Copper Queen smelter and septic systems, 6 targeted groundwater samples were collected in the City of Douglas area. Since pH-field, temperature-field, and Na were the only parameters typically exceeding the $CI_{0.95}$, there appeared to be no groundwater quality impacts from these land uses (**Table 15**). However, these $CI_{0.95}$ exceedances, along with very low levels of Ca and Mg, suggest that groundwater in the Greater Douglas area is being subjected to natural softening by cation exchange with Na ions.

- Three targeted groundwater quality samples were collected in the vicinity of Mule Gulch in an attempt to discern any impacts stemming from mine tailing dumps and the Bisbee Sewage Disposal Plant (**Figure 17**). With 2 SO_4 levels exceeding the $CI_{0.95}$ and 3 pH-field levels below the $CI_{0.95}$, it appears that mine tailings may be impacting groundwater quality in the area (**Table 16**). This relationship was further supported by a significant correlation ($p=0.01$) by comparing the SO_4 levels of 4 wells with distance from the well closest to the mine tailings (**Figure 18**). In addition, potential impacts are shown from the Bisbee Sewage Disposal Plant as the well closest to the facility had a NO_3-N level exceeding the $CI_{0.95}$.

- Two targeted groundwater quality samples were collected near the Town of McNeal because a 1990 ADWR study found F levels above the Primary MCL. ADEQ sampling results suggest that F levels in the McNeal area are elevated in comparison to $CI_{0.95,}$ sometimes exceeding Secondary MCL levels. As such, the 1990 ADWR results that exceeded Primary MCL levels may be an accurate reflection of F levels in the McNeal area (Rascona, 1995).

- A single targeted sample was collected to the east of the Bisbee-Douglas International Airport. This sample had 13 parameter levels that exceeded the DGB $CI_{0.95}$, many by several magnitudes (**Table 18**). The TDS level of 14,200 mg/l indicates that this well may be pumping groundwater from what appears to be a limited geothermal anomaly.

Conduct a groundwater quality time-trend analysis using results from previous studies for baseline data:

A limited groundwater quality time-trend analysis based on historical data from 7 wells sampled by ADWR/USGS in 1987 and ADEQ in 1995/96 was conducted in the DGB (**Figure 19**). The results indicated that many of the 12 parameters had higher levels in 1995-96 than 1987, though only NO_3-N and K were significantly higher. In contrast, pH-field was significantly lower in 1995-96 than 1987 (**Table 19**). Using linear regression, the two data sets were significantly correlated at $p = 0.01$ and the variation was approximately 1% (**Figure 20**).

Establish an ambient monitoring index well network for long-term examination of temporal groundwater quality trends:

An ambient groundwater monitoring well network of 16 index wells, 1 located in every other township forming a “checkerboard” pattern, was established in the DGB (**Table 20** and **Figure 21**). Of the 16 wells, 7 were previously sampled by ADWR in 1987 in order to “jump start” the groundwater quality comparisons over time in the DGB. The ADEQ ambient index well groundwater monitoring network in the DGB should be resampled more frequently than every 8 years, based on the time-trend analysis provided in this report. Of particular concern are the significantly increasing NO_3-N levels in conjunction with the continued development taking place in the basin.

11. DISCUSSION

Although regional groundwater quality conditions generally support drinking water uses in the DGB, there are several indications that groundwater quality should be closely monitored to avoid future problems. There are 4 areas of particular concern:

- TDS levels in the DGB;
- SO_4 levels in the Mule Gulch area;
- F levels in the DGB, particularly in the McNeal area; and
- Nitrate levels in the DGB, particularly in the Elfrida and Mule Gulch areas.

TDS levels in the DGB. The source of most of the dissolved solids contained in the DGB groundwater are thought to be a result of the alluvium minerals that comprise the valley fill. The cations especially, are likely to be derived directly from solution of minerals in rocks and soil; anions may, in a large part, come from nonlithologic sources (Hem, 1970). The opportunity for groundwater to dissolve minerals from rock and soil increases with time, so TDS levels in groundwater should be expected to increase uniformly with depth and distance from recharge areas. Such TDS levels are difficult to predict, however, since the alluvium is not homogenous and contains materials with different compositions and solubilities (Coates and Cushman, 1955). The occasionally high TDS levels found in the alluvial aquifer may be related to the presence of evaporite beds, such as the gypsum deposits that are sometimes encountered in the DGB.

SO_4 levels near Mule Gulch. Elevated SO_4 levels were found where Mule Gulch leaves the bedrock and enters the alluvium of the DGB. It appears that the mining wastes in the Mule Gulch area are impacting the groundwater in a similar manner as has been documented in the Bisbee-Naco area within the Upper San Pedro Groundwater Basin. The USGS hypothesized that the elevated SO_4 levels (650 - 850 mg/l) sampled in the aquifer between the communities of Bisbee and Naco might be the result of groundwater recharging through an upgradient mine-tailings pond (Litten, 1987). The mine tailings dumps found along the upper reaches of Mule Gulch could have a similar negative recharge affect on groundwater quality. Low pH values in this area support this conclusion.

F levels in the DGB. Fluoride is another concern in the DGB. A recent study by ADWR found many F levels over the Primary MCL of 4 mg/l, especially in the vicinity of McNeal (Rascona, 1993). The 5 wells sampled nearest this community had F levels ranging from 5.6 - 15 mg/l, all of which exceeded the Primary MCL, some by several magnitudes. A conversation with the author of the ADWR report revealed that the instrument ADWR had used to measure F levels in the study may have malfunctioned. The author was concerned with the accuracy of some measurements, particularly the elevated F levels around McNeal. ADEQ results of wells sampled in the McNeal area revealed F levels frequently exceeded the Secondary MCL of 2.0 mg/l but no samples exceeded the Primary MCL. Furthermore, F levels in the DGB were generally acceptable with 8 of the 51 wells sampled by ADEQ exceeding Secondary MCL levels and none exceeding Primary MCL levels. ADEQ sample results suggest that the F levels collected by ADWR in their 1993 study might be an accurate reflection of F levels in the McNeal area. Future studies should carefully examine F levels, particularly in the McNeal area.

Nitrate levels in the DGB. Nitrate levels in the DGB are another concern. Although only 1 of the 51 wells sampled had a nitrate (as N) level over the 10.0 mg/l Primary MCL, 2 trends suggest this parameter is becoming a greater threat to the groundwater quality in the DGB. A time-trend statistical analysis conducted on samples collected from 7 wells by ADWR in 1987 and resampled by ADEQ in 1995-96 indicated that nitrate levels have significantly increased. Furthermore, an examination of potential impacts from septic systems and irrigated agricultural practices in the Elfrida area revealed that nitrate level samples collected from targeted wells frequently exceeded the nitrate upper 95% Confidence Intervals established from random sampling within the DGB. Previous studies indicate that nitrate levels in the DGB have historically been low; only 1 out of 112 wells sampled in the late 1940s/early 1950s exceeded the nitrate (as N) Primary MCL (Coates and Cushman, 1955). These authors thought that the nitrate present in the groundwater of the DGB probably was derived from sources other than contamination by human and animal wastes, and this theory should be considered in future DGB nitrate studies. The positive nitrate parameter level correlation with levels of major ions in the DGB may support this non-human/animal waste source of nitrate, as nitrate levels in other studies usually are negatively-correlated with major ions (Towne and Yu, 1998). Nitrate isotope analysis could be used in future studies to assist in determining the source of nitrate in the groundwater.

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